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# The Fedorov–Groth law revisited: complexity analysis using mineralogical data

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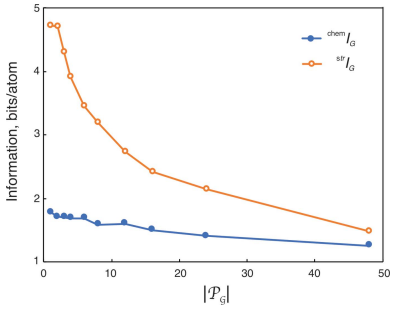
The Fedorov–Groth law points out that, on average, chemical simplicity corresponds to higher symmetry, and chemically complex compounds usually have lower symmetry than chemically simple compounds. Using mineralogical data, it is demonstrated that the Fedorov–Groth law is valid and statistically meaningful, when chemical complexity is expressed as the amount of Shannon chemical information per atom and the degree of symmetry as the order of the point group of a mineral.

## 1. Introduction

The relations between the symmetry of crystalline solids and their chemical composition is one of the interesting topics in crystallography, and was the subject of studies by the two prominent crystallographers of the XIX–XXth centuries, Paul Heinrich von Groth (1843–1927; Munich, Germany) and Evgraf Stepanovich Fedorov (1856–1919; St Petersburg, Russia). Groth and Fedorov were close friends and colleagues and both were heavily involved in shaping crystallography as a science prior to the discovery of X-ray diffraction by crystals (Paufler & Filatov, 2020). First Fedorov (1913, 1914) and then Groth (1921) pointed out that, in general, the symmetry of crystalline compounds correlates with their chemical complexity. Less complex compounds (*e.g.* elements) tend on average to have higher symmetries than compounds consisting of two elements *etc.* This empirical observation was considered in Russian literature as the Fedorov–Groth law (Boldyrev, 1934; Yushkin *et al.*, 1987; Talanov, 2007), and both Fedorov and Groth pointed out that it has an 'approximate' character only, *i.e.* it has a statistical nature that allows exceptions, but works on a global scale. As far as we know, there have been no attempts to scrutinize this law using modern crystallographic data, and this is the aim of the present communication which presents such an analysis for minerals using recently formulated concepts of structural and chemical complexity of crystals (Krivovichev, 2012, 2013, 2014, 2016).

## 2. Methods

For the study, a total of 5349 data sets on chemical compositions of all mineral species approved by the International Mineralogical Association (IMA) up to 2020 (Pasero, 2020) and 4529 data sets on the crystal structures of minerals were considered (for some 820 mineral species, the crystal structures are still unknown for different reasons that cannot be

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considered herein). The crystal chemical formulae of minerals have been rewritten in a canonical way in order to determine the minimal set of species-defining constituents (*i.e.* chemical elements that are dominant in particular sites in a crystal structure). It should be noted that the assignment of an element as species-defining is determined by the rules of the definition of new mineral species given by the IMA (Mandarino *et al.*, 1984; Nickel, 1992, 1995). In isovalent and heterovalent series, only essential chemical elements were taken into account, without consideration of isomorphic substitutions (see also Krivovichev & Charykova, 2013*a*,*b*; Krivovichev *et al.*, 2018*b*). The crystal structure data have been extracted from the Inorganic Crystal Structure Database (ICSD; Hellenbrandt, 2004), the *American Mineralogist* crystal structure database (Downs & Hall-Wallace, 2003) and original publications (in the cases when the data were not found in the databases). For each mineral, the following data have been obtained: (i) the order $|\mathcal{P}_G|$ of the point group $\mathcal{P}_G$ of the space group $\mathcal{G}$ [taken here as a measure of symmetry degree; we recall that the values possible for crystalline compounds are 1, 2, 3, 4, 6, 8, 12, 16, 24 and 48 (Wondratschek & Müller, 2004)]; (ii) information-based chemical and structural complexity parameters defined as follows (Krivovichev, 2012, 2013, 2014, 2016; Krivovichev *et al.*, 2018*a*).

The chemical complexity was evaluated by the amounts of chemical information per atom ($^{\rm chem}I_{\rm G}$) and per formula unit, f.u. ($^{\rm chem}I_{\rm G,total}$), as suggested in the work of Siidra *et al.* (2014). Following this approach, for the idealized chemical formula of a mineral or inorganic compound, $\mathrm{E}^{(1)}{}_{c1}\mathrm{E}^{(2)}{}_{c2}\ldots\mathrm{E}^{(k)}{}_{ck}$, where $\mathrm{E}^{(i)}$ is an $i$th chemical element in the formula and $c_i$ is its integer coefficient, the chemical information can be calculated as follows:

$$^{\rm chem}I_{\rm G} = -\sum_{i=1}^{k} p_i \log_2 p_i \quad \text{(bits/atom)} \qquad (1)$$

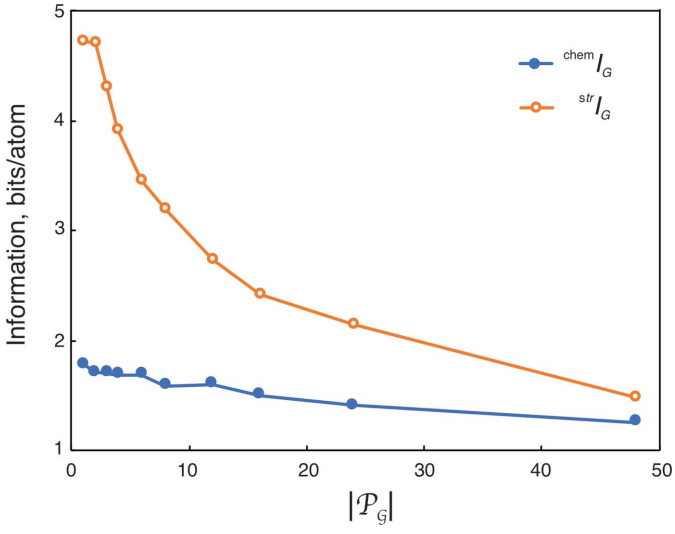


**Figure 1**
The dependence of average chemical ($^{\rm chem}I_{\rm G}$) and structural ($^{\rm str}I_{\rm G}$) Shannon information amounts for minerals on the order of the point group, $|\mathcal{P}_\mathcal{G}|$.

**Table 1**
Information-based mean chemical ($^{\rm chem}I_{\rm G}$) and structural ($^{\rm str}I_{\rm G}$) complexities (bits/atom) of minerals separated according to the orders of their point groups, $|\mathcal{P}_\mathcal{G}|$.

$n$ = number of minerals taken into account; M = arithmetic mean; SEM = standard error of the mean.

| | | $^{\rm chem}I_{\rm G}$ (bits/atom) | | | $^{\rm str}I_{\rm G}$ (bits/atom) | |
|---|---|---|---|---|---|---|
| $\lvert\mathcal{P}_\mathcal{G}\rvert$ | $n$ | M | SEM | $n$ | M | SEM |
| 1 | 65 | 1.78 | 0.03 | 49 | 4.73 | 0.21 |
| 2 | 742 | 1.71 | 0.01 | 628 | 4.71 | 0.04 |
| 3 | 52 | 1.70 | 0.04 | 40 | 4.30 | 0.22 |
| 4 | 1956 | 1.69 | 0.01 | 1691 | 3.91 | 0.03 |
| 6 | 377 | 1.69 | 0.02 | 341 | 3.46 | 0.07 |
| 8 | 910 | 1.59 | 0.01 | 759 | 3.19 | 0.04 |
| 12 | 465 | 1.60 | 0.02 | 400 | 2.73 | 0.06 |
| 16 | 200 | 1.50 | 0.03 | 173 | 2.42 | 0.10 |
| 24 | 315 | 1.41 | 0.03 | 209 | 2.15 | 0.07 |
| 48 | 267 | 1.26 | 0.07 | 239 | 1.49 | 0.02 |

$$^{\rm chem}I_{\rm G,total} = e^{\rm chem}I_{\rm G} = -e\sum_{i=1}^{k} p_i \log_2 p_i \quad \text{(bits/f.u.)} \qquad (2)$$

where $k$ is the number of different elements in the formula and $p_i$ is the random-choice probability for an atom of the $i$th element, that is:

$$p_i = c_i/e \qquad (3)$$

where $e$ is the total number of atoms in the chemical formula:

$$e = \sum_{i=1}^{k} c_i. \qquad (4)$$

The amounts of structural Shannon information per atom ($^{\rm str}I_{\rm G}$) and per unit cell ($^{\rm str}I_{\rm G,total}$) were calculated according to the following equations:

$$^{\rm str}I_{\rm G} = -\sum_{i=1}^{k} p_i \log_2 p_i \quad \text{(bits/atom)} \qquad (5)$$

$$^{\rm str}I_{\rm G,total} = v^{\rm str}I_{\rm G} = -v\sum_{i=1}^{k} p_i \log_2 p_i \quad \text{(bits/cell)} \qquad (6)$$

where $k$ is the number of different crystallographic orbits in the structure and $p_i$ is the random-choice probability for an atom from the $i$th crystallographic orbit, that is:

$$p_i = m_i/v \qquad (7)$$

where $m_i$ is the multiplicity of a crystallographic orbit (*i.e.* the number of atoms of a specific Wyckoff site in the reduced unit cell), and $v$ is the total number of atoms in the reduced unit cell. For minerals with unknown positions of H atoms, the procedure of H correction was applied by introducing surrogate H sites (Pankova *et al.*, 2018).

## 3. Results

Information-based chemical and structural complexity parameters for minerals have been separated into ten groups according to the order of their point groups ($|\mathcal{P}_\mathcal{G}|$) which ranges from 1 (lowest symmetry) for triclinic minerals to 48

(highest symmetry) for cubic minerals. The results are summarized in Table 1 and depicted graphically in Fig. 1. The best fitting was obtained for the ${}^{\rm chem}I_{\rm G}$ versus $|\mathcal{P}_{\mathcal{G}}|$ and ${}^{\rm str}I_{\rm G}$ versus $|\mathcal{P}_{\mathcal{G}}|$ relations by means of the exponential functions:

$${}^{\rm chem}I_{\rm G} = 1.122 + 0.634 \times \exp(-|\mathcal{P}_{\mathcal{G}}|/30.956),\ \text{bits/atom} \quad (R^2 = 0.979) \tag{8}$$

$${}^{\rm str}I_{\rm G} = 1.580 + 3.532 \times \exp(-|\mathcal{P}_{\mathcal{G}}|/10.718),\ \text{bits/atom} \quad (R^2 = 0.987). \tag{9}$$

The relations obtained indicate that there are strong relations (confidence level > 0.99) between the chemical and structural complexities (${}^{\rm chem}I_{\rm G}$ and ${}^{\rm str}I_{\rm G}$) and the orders of the point groups ($|\mathcal{P}_{\mathcal{G}}|$). No good correlations have been obtained for the amounts of chemical and structural information per formula and per reduced unit cell, respectively, versus the $|\mathcal{P}_{\mathcal{G}}|$ values, which is not surprising, since point-group symmetry of a system is not a function of its size (in this case, the number of atoms in a reduced unit cell).

## 4. Summary

The observed strong negative correlation between the amount of chemical information per atom, ${}^{\rm chem}I_{\rm G}$, and the order of the point group, $|\mathcal{P}_{\mathcal{G}}|$, indicates that the Fedorov–Groth law is indeed valid and has a statistical meaning. Chemical simplicity measured as an amount of Shannon information per atom on average corresponds to higher symmetry measured as an order of the point group of a mineral. On the other hand, the observed correlation between ${}^{\rm str}I_{\rm G}$ and $|\mathcal{P}_{\mathcal{G}}|$ is not surprising at all, since the ${}^{\rm str}I_{\rm G}$ is exactly symmetry-sensitive (Krivovichev, 2012). Krivovichev *et al.* (2018*a*) demonstrated that, on average, there exists a positive, though non-trivial, correlation between ${}^{\rm chem}I_{\rm G}$ and ${}^{\rm str}I_{\rm G}$ for minerals.

It is important to note that the majority of minerals are stable under ambient conditions and therefore the data are not affected seriously by the existence of high-pressure and high-temperature modifications, as one would expect from the analysis of the data for all known inorganic compounds.

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